Calculation of Energy Levels for Internal Torsion and Overall Rotation.[*]

I. CH_3BF_2 Type Molecules.

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Abstract

Methods are described for calculating the energy levels for
the overall rotation and internal torsion of molecules consisting
of a rigid symmetrical top attached to a rigid asymmetrical frame-
work in such a way that the symmetry axis of the top coincides with
a principal axis of the molecule. Probable examples are nitromethane
and CH_3BF_2. Matrix perturbation methods are employed to obtain
finite rotational secular equations valid in each of the cases:
low barrier, high barrier, low asymmetry. These secular equations
are modifications of the ordinary Wang equation for the rigid
asymmetric rotor and can usually be solved by the continued fraction
method. The symmetry groups applicable to this problem are also
discussed.

Molecules such as CH_3BF_2 or nitromethane[1] (CH_3NO_2) may show overall rotation, internal torsion of the methyl group relative to the NO_2 group, and vibration.

[1] Microwave spectra due to these motions have been recently reported for nitromethane by Tannenbaum, Johnson, Myers, and Gwinn, J. Chem. Phys. 22, 949 (1954).

For the purpose of treating the overall rotation and internal torsion, it is convenient to think of the BF_2 or NO_2 group as a rigid framework to which is attached a symmetrical top (CH_3) which may rotate or vibrate about an axis colinear with a principal axis of inertia of the whole molecule. Furthermore, the three principal moments of inertia of the whole molecule are all different and are uninfluenced by the internal orientation of the attached top. The calculation of the rotational and internal torsional energy levels of this class of molecules is the subject of the present paper.[2]

[2] The class treated here is in some ways simpler than the case of methyl alcohol which has been thoroughly studied by Dennison and coworkers (see Ivash and Dennison, J. Chem. Phys. 21, 1804 (1954)) but the approach differs somewhat.

Model and Coordinates

The model then consists of two connected rigid[3] bodies, one (the top)

[3] For a discussion of vibrations in molecules of this type, see B. L. Crawford, Jr. and E. B. Wilson, Jr., J. Chem. Phys. 9, 323 (1941).

having two equal principal moments of inertia about axes perpendicular to a principal axis of the whole molecule. There are four degrees of freedom, three for overall rotation and one for rotation of the top about its unique axis. See Fig. 1.

Let x,y,z be moving cartesian axes rigidly attached to the framework part of the molecule and coincident with the principal axes of inertia of the whole molecule (origin is at center of mass of whole molecule). The z axis will coincide with the symmetry axis of the top. The three Eulerian angles θ, φ, and χ of x,y,z relative to space-fixed axes will describe the overall orientation of the molecule, while the angle α will give the relative orientation of top and framework.

The Hamiltonian

The kinetic energy has previously been written as[4]

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[4] B. L. Crawford, Jr., J. Chem. Phys. $\underline{8}$, 273 (1940).

$$2T = I_x \omega_x^2 + I_y \omega_y^2 + I_z \omega_z^2 + I_\alpha \dot{\alpha}^2 + 2I_\alpha \dot{\alpha} \omega_z \qquad (1)$$

in which I_α is the moment of inertia of the top about its symmetry axis, I_x, I_y, I_z are the principal moments of the entire molecule, and ω_x, ω_y, ω_z are components of angular velocity of the framework along x,y,z. It has been usual[5] to eliminate the cross-product terms by means of a transformation,

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[5] See K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. $\underline{10}$, 428 (1942).

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but this will not be done in this treatment.

To obtain the Hamiltonian form, use the definitions of the momenta:

$$p = \partial T / \partial \dot{\alpha}, \ P_x = \partial T / \partial \omega_x, \ \text{etc.} \qquad (2)$$

This leads in the usual way to the form

$$H = AP_x^2 + BP_y^2 + CP_z^2 + Fp^2 - 2CpP_z + V(\alpha) \qquad (3)$$

in which all angular momenta are in units $\hbar = h/2\pi$ and

$$A = \frac{1}{2}\hbar^2/I_x, \ B = \frac{1}{2}\hbar^2/I_y, \ C = \frac{1}{2}\hbar^2/(I_z-I_\alpha), \ F = \frac{1}{2}\hbar^2 I_z/\left[I_\alpha(I_z-I_\alpha)\right] \tag{4}$$

$V(\alpha)$ is the potential energy restricting the internal rotation. In the model used here, the coefficients are all constants. Note that C involves the moment of inertia of the framework part alone while F contains the reduced moment of the two parts of the molecule.

The quantities P_x, P_y and P_z were defined in Eq. (2) but by using the basic definition of angular momentum it is easy to show that they are equal to the components of the total angular momentum of the molecule (in units $h/2\pi$), including the contributions arising from any internal rotation of the top. Similarly it can be shown that p is the total contribution of the motion of the top atoms to the z component of angular momentum, including both the internal and overall motions.

This classical Hamiltonian becomes a quantum mechanical operator or alternately a matrix by regarding P_x, P_y, P_z and p as operators or matrices. The commutation rules[6] are

^{6} O. Klein, Zeits. f. Physik 58, 730 (1929).

$$P_j P_k - P_k P_j = -iP_\ell, \quad (j,k,\ell = x,y,z \text{ in cyclic order}) \tag{5}$$

and

$$pP_j - P_j p = 0 \qquad j = x,y,z \tag{6}$$

The first rule is the standard one for the components of angular momenta along molecule-fixed axes while the second follows from the fact that, as an operator

$$p = - i(\partial/\partial\alpha)_{\theta,\varphi,\chi} \tag{7}$$

whereas the P_i's do not involve α.

By inserting in H the expressions for the P_i in terms of p_θ, p_φ and p_χ and in turn treating these latter momenta as differential operators, the Schrödinger wave equation in the variables $\theta, \varphi, \chi, \alpha$ could be written down, but this is not necessary for the solution of the problem.

To simplify the later equations, let

$$\mathcal{H}' = \left[H - D(P_x^2 + P_y^2 + P_z^2)\right]/(C-D) \tag{8}$$

in which
$$D = \frac{1}{2}(A + B) \tag{9}$$

Then

$$\mathcal{H}' = b(P_x^2 - P_y^2) + P_z^2 - dpP_z + fp^2 + V'(\alpha) \tag{10}$$

with

$$b = \frac{1}{2}(A - B)/(C - D)$$

$$d = 2C/(C - D)$$

$$f = F/(C - D) \tag{11}$$

$$V' = V/(C - D)$$

Then if Λ' is an eigenvalue of $\mathcal{H}'$, the energy is given by

$$W = J(J + 1)D + (C - D)\Lambda' \tag{12}$$

$\mathcal{H}'$, as well as H, is diagonal in J and M so only one JM block need be considered at a time.

Symmetry Considerations

It is well known that the rigid asymmetric rotor wave equation is invariant under the group of 180° rotations about each of the principal axes. These operations variously change the signs of the P_i, which leaves the energy

expression unaltered. In the present problem the cross-term in pP_z is not invariant unless p changes sign when P_z does. If the potential energy $V(\alpha)$ is an even function of α, then the four operations E, C_x, C_y, C_z whose effects are listed below will still leave H invariant and will form a group (the "four-group") as before.

Table I. Effect of Four-Group Symmetry Operations

E	C_x	C_y'	C_z
$P_1 \longrightarrow P_1$	$P_x \longrightarrow P_x$	$P_y \longrightarrow P_y$	$P_z \longrightarrow P_z$
	$P_{y,z} \longrightarrow -P_{y,z}$	$P_{x,z} \longrightarrow -P_{x,z}$	$P_{x,y} \longrightarrow -P_{x,y}$
$p \longrightarrow p$	$p \longrightarrow -p$	$p \longrightarrow -p$	$p \longrightarrow p$
$(\alpha \longrightarrow \alpha)$	$(\alpha \longrightarrow -\alpha)$	$(\alpha \longrightarrow -\alpha)$	$(\alpha \longrightarrow \alpha)$
$(\theta \longrightarrow \theta)$	$(\theta \longrightarrow \pi-\theta)$	$(\theta \longrightarrow \pi-\theta)$	$(\theta \longrightarrow \theta)$
$(\varphi \longrightarrow \varphi)$	$(\varphi \longrightarrow \pi+\varphi)$	$(\varphi \longrightarrow \pi+\varphi)$	$(\varphi \longrightarrow \varphi)$
$(\chi \longrightarrow \chi)$	$(\chi \longrightarrow 2\pi-\chi)$	$(\chi \longrightarrow \pi-\chi)$	$(\chi \longrightarrow \pi+\chi)$

Consequently every solution of the wave equation will belong to one of the four species A, B_x, B_y, B_z of this group[7] as in the case of the asymmetric

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[7] See G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. __11__, 27 (1943).

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rotor, but here the part of the function involving α must be included. Further, any secular equation or energy matrix can be factored into at least four factors by using the above symmetry.

Often $V(\alpha)$ will possess additional symmetry properties. For example, in nitromethane, it presumably is invariant under $\alpha \longrightarrow \alpha + 2\pi k/6$, where $k = 0,1,2,3,4,5$. In addition, $\alpha \longrightarrow (2\pi k/6) - \alpha$ should also leave V unchanged. These operations are isomorphous with the point group C_{6v} but this group is not here used in the same way as when group theory is applied to the vibration problem.

The symmetry of $V(\alpha)$ cannot be indiscriminately applied to E because p appears in the cross term. However, the "rotations" $\alpha \longrightarrow \alpha + 2\pi k/s$ (here $s = 6$) do leave H invariant. So do the "reflections" $\alpha \longrightarrow (2\pi k/s) - \alpha$ if simultaneously $P_z \longrightarrow -P_z$. The four-group operations listed earlier and the s internal rotations $\alpha \longrightarrow \alpha + 2\pi k/s$ generate a group of $4s$ operations. Table II shows the result when $s = 3$, in which case the group is isomorphous with the group C_{6v}.

Table II. Character Table for Case $s = 3$.

Class	E	$2C_3$	$3C_x C_3$	C_z	$2C_z C_3$	$3C_y C_3$
A	1	1	1	1	1	1
B_z	1	1	-1	1	1	-1
E_1	2	-1	0	2	-1	0
B_x	1	1	1	-1	-1	-1
B_y	1	1	-1	-1	-1	1
E_2	2	-1	0	-2	1	0

The one-dimensional species are here labelled so that they correspond to the species for the subgroup V. The degenerate species E_1 would become $A + B_z$, in the subgroup while E_2 would yield $B_x + B_y$.

The case s = 6 is easily constructed from the above table because the new group is obtained by introducing the additional operation C_6^3 which causes $\alpha \longrightarrow \alpha + \pi$. This commutes with all operations above so the new group has twice as many classes and twice as many species as the old. See Table III.

Table III. Character Table for Case s = 6.

	E	$2c_3$	$3c_xc_3$	c_z	$2c_zc_3$	$3c_yc_3$	c_6^3	$2c_3c_6^3$	$3c_xc_3c_6^3$	$c_zc_6^3$	$2c_zc_3c_6^3$	$2c_yc_3c_6^3$
A_e	1	1	1	1	1	1	1	1	1	1	1	1
B_{ze}	1	1	-1	1	1	-1	1	1	-1	1	1	-1
E_{1e}	2	-1	0	2	-1	0	2	-1	0	2	-1	0
B_{xe}	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
B_{ye}	1	1	-1	-1	-1	1	1	1	-1	-1	-1	1
E_{2e}	2	-1	0	-2	1	0	2	-1	0	-2	1	0
A_o	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
B_{zo}	1	1	-1	1	1	-1	-1	-1	+1	-1	-1	+1
E_{1o}	2	-1	0	2	-1	0	-2	1	0	-2	1	0
B_{xo}	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1
B_{yo}	1	1	-1	-1	-1	1	-1	-1	1	1	1	-1
E_{2o}	2	-1	0	-2	1	0	-2	1	0	2	-1	0

These higher symmetries permit further factoring of the secular equation or energy matrix if the expansion functions are chosen to have symmetries in accord with the various species.

The dipole moment μ for this model would ordinarily be along the z axis. If this is the case, μ will have the symmetry B_z in Table II and in the case s = 6 it will belong to B_{ze}. Consequently, for this case, the selection rules for dipole absorption will be (s = 3): $A \longleftrightarrow B_z$, $B_x \longleftrightarrow B_y$, $E_1 \longleftrightarrow E_1$, $E_2 \longleftrightarrow E_2$. The rules will apply for the case s = 6 with the additional condition that e species go only into e species, and o species into o species.

Nuclear permutation effects will be governed by the symmetry also. The subgroup which governs the exchange of the oxygen atoms in nitromethane or the fluorines in CH_3BF_2 consists of E and $C_z C_6^3$ since to exchange these atoms requires that $\alpha \longleftrightarrow \alpha + \pi$, $\chi \longleftrightarrow \chi + \pi$, which is $C_z C_6^3$. A_e, B_{ze}, E_{1e}, B_{xo}, B_{yo}, E_{2o} are even, the other species odd to this operation. Therefore only the first set can occur in nitromethane (with ^{16}O). In CH_3BF_2 these species will have three times the fluorine spin weight of the others. The operations C_3, C_3^2 exchange two pairs of H atoms in the above molecules. All the non-degenerate species are of species A in this subgroup, all the degenerate species will be degenerate in the subgroup. The two kinds of levels will then have equal proton spin weight.

The Energy Matrix

If the asymmetry (b) were zero and there were no barrier (V'), the reduced Hamiltonian $\mathcal{H}'$would be

$$P_z^2 - dpP_z + fp^2 \tag{13}$$

which yields a diagonal matrix with the basis functions

$$S_{JKM}(\theta, \varphi) \, e^{iK\chi} e^{im\alpha} \tag{14}$$

in which S is the θ, φ factor of the symmetric rotor wave function and

$$K = 0, \pm 1, \pm 2, \ldots \pm J \; ; \; m = 0, \pm 1, \pm 2, \ldots \infty . \tag{15}$$

These functions may be used to set up a matrix for the general form of $\mathcal{H}'$, i.e. the true wave functions may be expanded in terms of the functions above. The asymmetry term in $\underline{b}$ will give off-diagonal elements the same as those which occur with the rigid asymmetric rotor (with C calculated for framework only). The barrier potential V' is usually assumed to be of the form

$$V' = \frac{1}{2} V_o' (1 - \cos s\, \alpha) = \frac{1}{2} V_o' - \frac{1}{4} V_o' (e^{is\alpha} + e^{-is\alpha}) \tag{16}$$

in which s is the number of equivalent minima and $(C-D)V_o' = V_o$ is the barrier height. The barrier will also introduce off-diagonal elements. The matrix for $\mathcal{H}'$ will then have the non-vanishing elements[8]

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[8] See ref. 7 for the matrix elements of P_x, P_y, and P_z.

$$\mathcal{H}_{Km,Km} = \mathcal{H}'_{Km,Km} - \frac{1}{2} V_o' = K^2 - dmK + fm^2$$

$$\mathcal{H}_{K,m;K\pm 2,m} = b_{K,K\pm 2} = \frac{1}{2} b \left\{ \left[J^2 - (K\pm 1)^2 \right] \left[(J+1)^2 - (K\pm 1)^2 \right] \right\}^{\frac{1}{2}} \tag{17}$$

$$\mathcal{H}_{K,m;K,m\pm s} = -\frac{1}{4} V_o' = \mathcal{J}$$

Here the constant $\frac{1}{2} V_o'$ has been incorporated so that the eigenvalues of $\mathcal{H}$ are related to those of $\mathcal{H}'$ by

$$\mathcal{A}' = \mathcal{A} + \frac{1}{2} V_o' \tag{18}$$

Unless the barrier height is zero, this form of $\mathcal{H}$ corresponds to an infinite secular equation. Note, however, that there are no elements connecting even with odd K values so that the secular equation factors into one for even and one for odd K values. (This is part of the factoring into different symmetry species.)

Case of Free Internal Rotation

When the barrier height is zero, $\mathcal{F} = -\frac{1}{4} V_0' = 0$ and the energy matrix becomes diagonal in m. The secular equation therefore factors into one block for each value of m, as well as into even and odd K factors.

The secular equation for a given value of J,M,m has the elements

$$(K|K) = K^2 - dmK - \lambda \; ;$$

$$(K|K \pm 2) = b_{K,K\pm2} = \frac{1}{2} b \left\{ \left[J^2 - (K\underline{\pm}1)^2 \right] \left[(J+1)^2 - (K\underline{\pm}1)^2 \right] \right\}^{\frac{1}{2}} \qquad (19)$$

The energy W is then related to the roots λ by the equation (see Eq. 12).

$$W = J(J + 1)D + \frac{1}{2} V_0 + Fm^2 + (C-D)\lambda \qquad (20)$$

This secular equation is similar to the Wang[9] equation for the ordinary

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[9] S. C. Wang, Phys. Rev. $\underline{34}$, 243 (1929).

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rigid asymmetric rotor except for the added term -dmK on the diagonal. This term spoils the additional factoring possible in the rigid case.

As an example, consider the case J = 5, K even. This factor becomes

$$\begin{vmatrix} 16 + 4\,md - \lambda & 6\sqrt{3}\,b & 0 & 0 & 0 \\ 6\sqrt{3}\,b & 4 + 2\,md - \lambda & \sqrt{210}\,b & 0 & 0 \\ 0 & \sqrt{210}\,b & -\lambda & \sqrt{210}\,b & 0 \\ 0 & 0 & \sqrt{210}\,b & 4 - 2\,md - \lambda & 6\sqrt{3}\,b \\ 0 & 0 & 0 & 6\sqrt{3}\,b & 16 - 4\,md - \lambda \end{vmatrix} = 0 \tag{21}$$

For each non-vanishing value of $|m|$, there will be two identical such equations, so all levels are doubly degenerate unless $m = 0$. In the latter case, the ordinary rigid rotor levels are obtained, except that the moment of inertia about the z axis is the moment of the framework group $(I_z - I_\alpha)$ as already seen.

The energy levels in the free rotation case must of course conform to the symmetry restrictions given for the general case. Thus, with $s = 3$ or 6, if m is not a multiple of 3, the symmetry is one of the degenerate E species. If m is a multiple of 3, the levels involve A or B species which would be split into non-degenerate components if there were a sufficient barrier. If K is even, the species may be A, B_z or E_1; if K is odd, B_x, B_y or E_2. If s = 6, the species further divide into even or odd (denoted by subscripts e and o) according as m is even or odd.

The selection rules for dipole radiation involve

$$\Delta J = 0, \pm 1 \tag{22}$$

as for the rigid asymmetric rotor. The symmetry requirements discussed earlier must also be met. If μ is along the z axis, K cannot change parity. The rule for m is

$$\Delta m = 0 \tag{23}$$

This follows from the fact that the dipole moment does not depend on α whereas the wavefunction involves α only through the factor

$$e^{im\alpha}$$

For small asymmetry the energy levels may be expanded in powers of b. For large values of the quantum number n, the diagonal elements of the secular equation will be large and the first terms in the expansion in powers of $\underline{b}$ may be adequate. Second-order perturbation theory then gives

$$\lambda = K^2 - md\, K + (b^2/8)\left\{\left[J^2 - (K-1)^2\right]\left[(J+1)^2-(K-1)^2\right]/(2K-md-2)\right\}$$
$$-(b^2/8)\left\{\left[J^2-(K+1)^2\right]\left[(J+1)^2-(K+1)^2\right]/(2K-md+2)\right\} + \ldots \qquad (24)$$

For very large values of m,

$$\lambda \longrightarrow K^2 - md\, K. \qquad (25)$$

For transitions with $\Delta J = 1$, $\Delta K = 0$, $\Delta m = 0$, the transitions with large values of m would then tend to converge (from both sides) to a band head. Of course the intensities of these higher members would tend to decrease because of the unfavorable Boltzmann factors.

Case of Low Barrier

If the barrier height V_0 is small but not negligible (compared with the quantity F), a useful solution can be obtained with the Van Vleck perturbation method.[10] The reduced hamiltonian matrix $\mathcal{H}$ of Eq. 17 is split into an

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[10] See E. C. Kemble, The Fundamental Principles of Quantum Mechanics, McGraw-Hill, New York, 1937. p. 394.

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unperturbed, completely diagonal matrix $\mathcal{H}^0$ with diagonal elements

$$\mathcal{H}^0_{Km,Km} = K^2 - dmK + fm^2 \qquad (26)$$

and a perturbation $\mathcal{H}^{\$}$ with elements

$$\mathcal{H}^{\$}_{K,m;K\pm2,m} = b_{K,K+2} = \frac{1}{2}b\left\{\left[J^2 - (K\pm1)^2\right]\left[(J+1)^2 - (K\pm1)^2\right]\right\}^{\frac{1}{2}} \tag{27}$$

$$\mathcal{H}^{\$}_{K,m;K,m\pm s} = \int = -\frac{1}{4}V_o' = -\frac{1}{4}V_o/(C - D)$$

The Van Vleck transformation reduces the elements off-diagonal in m to order $\int^2$. If these are then neglected, the secular equation becomes

$$(K|K) = K^2 - dmK + (1/s)\int^2\left\{(1/\left[Kd-(2m+s)f\right]) - (1/\left[Kd-(2m-s)f\right])\right\} - \lambda \tag{28}$$

$$(K|K\pm2) = b_{K,K+2}$$

This secular equation is similar in its properties to that for free rotation. It is not valid, however, for the case $m = \pm\frac{1}{2}s$, s even, because then a near degeneracy occurs. For this case, the unperturbed states with $m = \pm\frac{1}{2}s$ must both be taken into consideration. The equation then has the non-vanishing elements

$$(\tfrac{s}{2},K|\tfrac{s}{2},K) = K^2 - \frac{1}{2}d\,s\,K + (1/s)\left[\int^2/(Kd - 2sf)\right] - \lambda$$

$$(-\tfrac{s}{2},K|-\tfrac{s}{2},K) = K^2 + \frac{1}{2}d\,s\,K - (1/s)\left[\int^2/(Kd + 2sf)\right] - \lambda$$

$$(\tfrac{s}{2},K|-\tfrac{s}{2},K) = \int \tag{29}$$

$$(\tfrac{s}{2},K|\tfrac{s}{2},K\pm2) = b_{K,K+2}$$

$$(-\tfrac{s}{2},K|-\tfrac{s}{2},K\pm2) = b_{K,K+2}$$

Because of the symmetry $(\frac{s}{2}, K + \frac{s}{2}, K') = (-\frac{s}{2}, -K \mp \frac{s}{2}, -K)$ this larger secular equation can be factored into two factors, similar to the way in which the Wang equation is factored. This leads to a splitting of the degeneracy.

When m is not a multiple of $\frac{1}{2}$ s, the levels are inherently doubly degenerate for all barriers. For m a multiple of $\frac{1}{2}$ s the degeneracy is ultimately split at high enough barriers. With the approximation given here this splitting will not appear except for $m = \frac{1}{2}$ s. The higher the multiple of $\frac{1}{2}$ s the higher the order of perturbation required to demonstrate the splitting.

The quantum number m is no longer a good quantum number when there is a barrier but if V_o is small it can still be used to label the levels. The selection rule $\Delta m = 0$ is no longer exact and must be replaced by the rigorous symmetry selection rules given earlier.

High Barriers

If the barrier is sufficiently high so that the torsional levels of a given symmetry are widely spaced compared with the rotational levels, a different perturbation treatment is possible, in which the asymmetry and the coupling term are treated as perturbations by the Van Vleck procedure. This leads as before to a rotational secular equation. The unperturbed operator for the energy is

$$H_o = DP^2 + (C-D) P_z^2 + Fp^2 + V(\alpha) \tag{30}$$

while the perturbation operator is

$$H_1 = \frac{1}{2} (A-B)(P_x^2 - P_y^2) - 2CpP_z \tag{31}$$

H_o can be diagonalized with the basis functions

$$S_{JKM}(\theta, \varphi)\, e^{iK\chi} U_{v\varkappa}(\alpha) \tag{32}$$

in which symmetric rotor functions are used as before and the U's are eigen-functions of

$$\left[Fp^2 + V(\alpha) \right] U_{v\varkappa} = E_{v\varkappa}\, U_{v\varkappa} \tag{33}$$

The torsional states are described by the quantum numbers $v\varkappa$, where v is the principal quantum number of the vibrational level, and $\varkappa$ is a degeneracy index.

For the potential function of equation (16), the non-degenerate ($\varkappa = 0$) eigenvalues of the torsional equation (33), which is now related to the Mathieu equation, can be obtained from published[11] tabulations through the

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[11] _Tables Relating to Mathieu Functions_, Columbia University Press, New York, 1951.

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connection

$$E_{vo} = \tfrac{1}{4}\, s^2\, F\, be_r(S) \text{ or } \tfrac{1}{4}\, s^2\, Fbo_r(S) \tag{34}$$

in which

$$S = (4/s^2)(V_o/F) \tag{35}$$

and the eigenvalues be_r and bo_r are given in the tables as functions of the parameter S. The values of the quantum number $v = 0,1,2,3,4$, etc. are identified respectively with the eigenvalues be_0, bo_2, be_2, bo_4, be_4, etc.

The degenerate levels have not been tabulated but can be calculated to any desired degree of accuracy by expansion of the eigenfunction in a Fourier series. Another method is, however, easier and is reasonably accurate for high barriers. Make the substitution

$$U_{v\mathcal{K}} = e^{i\mathcal{K}\,\alpha}\, u(\alpha) \tag{37}$$

in Eq. (33), where $\mathcal{K} = 0$, 1, or -1. The equation for u is then

$$\left[F p^2 + 2F\mathcal{K}p + F\mathcal{K}^2 + V \right] u = E_{v\mathcal{K}} u \tag{38}$$

If $\mathcal{K} = 0$, the equation gives the non-degenerate eigenvalues and their eigenfunctions, both of which are available as tabulations. If $\mathcal{K} = \pm 1$, the degenerate levels are obtained. But the terms involving $\mathcal{K}$ in Eq. (38) can be considered as perturbations on the $\mathcal{K} = 0$ case, if the barrier is high enough. The term in $\mathcal{K}^2$ obviously just subtracts from $E_{v\mathcal{K}}$. To the second-order the effect of the terms in $\mathcal{K}$ and $\mathcal{K}^2$ is

$$E_{v\mathcal{K}} = E_{vo} + F\mathcal{K}^2 + 4F^2\mathcal{K}^2 \sum_{v'}{}' \left| p_{vv'} \right|^2 / (E_{vo} - E_{v'o}) \tag{39}$$

in which the sum is over all the non-degenerate levels and

$$p_{vv'} = -i \int_0^{2\pi} U_{vo}^* \left(\partial U_{v'o} / \partial \alpha \right) d\alpha$$

$$= \sum_{m=-\infty}^{\infty} m A_{vm} A_{v'm} \Bigg/ \left\{ \sum_{m=-\infty}^{\infty} A_{vm}^2 \sum_{m=-\infty}^{\infty} A_{v'm}^2 \right\}^{\frac{1}{2}} \tag{40}$$

Here we have expanded the non-degenerate eigenfunctions as

$$U_{vo}(\alpha) = \sum_{m=-\infty}^{\infty} A_{vm}\, e^{im\mathcal{X}}$$

These Fourier coefficients may be found from the tabulations of reference 11 by the identification

$$A_{v,-sk} = A_{v,sk} = (-1)^k De_{2k}(S), \qquad k \neq 0$$

$$A_{v,o} = 2De_o(S) \qquad\qquad \text{for even } v$$

$$\dot{A}_{v,-sk} = -\dot{A}_{v,sk} = (-1)^k Do_{2k}(S) \qquad\qquad \text{for odd } v$$

The perturbation H_1 of Eq. (31) now needs to be introduced by the Van Vleck procedure. However, for the degenerate torsional states, it is convenient to combine this perturbation with that given above, yielding the secular equation

$$(K|K) = K^2 - d'\mathcal{K}K - \Lambda''$$

$$(K|K \pm 2) = \tfrac{1}{2} b' \left\{ \left[J^2 - (K \pm 1)^2 \right] \left[(J+1)^2 - (K \pm 1)^2 \right] \right\}^{\tfrac{1}{2}} \qquad (41)$$

with

$$W = J(J+1)D + E_{vo} + F'K^2 + \Lambda''(C'-D)$$

$$C' = C(1 + 4C\rho)$$

$$d' = 2C(1 + 4F\rho)/(C'-D) \qquad\qquad (42)$$

$$F' = F(1 + 4F\rho)$$

$$\rho = \sideset{}{'}\sum_{v'} |p_{vv'}|^2/(E_{vo} - E_{v'o})$$

$$b' = \tfrac{1}{2}(A-B)/(C'-D)$$

Very High Barriers

If the barrier V is sufficiently high, the lower energy levels should approximate those of a rigid rotor with moments of inertia I_x, I_y, I_z (not $I_z - I_\alpha$) and a harmonic torsional vibrator with a reduced moment of inertia

$$I_\alpha(I_z - I_\alpha)/I_z \tag{43}$$

and potential energy

$$\frac{1}{2}\,(d^2V/d\alpha^2)_o\,\alpha^2 \tag{44}$$

This result can be shown to follow from Eq. (41) and (42), since

$$4F\rho \longrightarrow -1 \tag{45}$$

for high barriers in which harmonic oscillator functions can be used for U_{vo} in Eq. (40).

The energy levels of rotation are then calculable by the standard methods used for the rigid asymmetric rotor. The torsional levels will be degenerate, three-fold if $n = 3$, six-fold if $n = 6$. However, some of this degeneracy may be eliminated when permutation symmetry occurs, as in nitromethane, whose levels will be only three-fold degenerate.

Case of Small Asymmetry

In cases for which the approximations so far described are all inadequate, another approach can be used,[12] as long as the asymmetry of the molecule is

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[12] This is very close to that introduced by Dennison, ref. 1.

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small. Let the reduced energy matrix $\mathcal{H}'$ of Eq. (10) be set up in terms of the basis functions

$$e^{iK\mathcal{X}}S_{JKM}(\theta,\varphi)\mathcal{V}_{vK}(\alpha) \tag{46}$$

in which S is a symmetric rotor function and $\mathcal{V}_{vK}(\alpha)$ is a periodic function of α which is an eigenfunction of the equation

$$\left[Fp^2 - dKp + V'(\alpha)\right]\mathcal{V}_{vK}(\alpha) = W_{vK}\mathcal{V}_{vK}(\alpha) \tag{47}$$

with eigenvalue W_{vK}. K enters as a parameter. The non-vanishing matrix elements for $\mathcal{H}'$ then become

$$\mathcal{H}'_{vK,vK} = K^2 + W_{vK}$$

$$\mathcal{H}'_{v,K;v',K\underline{+}2} = b_{K,K\underline{+}2} \, \Delta_{vK,v'K\underline{+}2} \tag{48}$$

where

$$\Delta_{v,K;v',K\underline{+}2} = \int_0^{2\pi} \mathcal{V}_{vK}^* \mathcal{V}_{v',K\underline{+}2} \, d\alpha, \tag{49}$$

which enters because $\mathcal{V}$'s for different K's are not orthogonal.

The existence of the terms off-diagonal in v spoils the factoring into v-blocks but these terms are normally small and can be reduced to lower order by a Van Vleck transformation. This yields a rotational secular equation

$$(K|K) = K^2 + W_{vK} - \mathcal{N}'$$

$$+ |b_{K,K+2}|^2 \sum_{v'}{}' |\Delta_{vK,v'K+2}|^2/(W_{vK} - W_{v'K+2})$$

$$+ |b_{K,K-2}|^2 \sum_{v'}{}' |\Delta_{vK,v'K-2}|^2/(W_{vK} - W_{v'K-2}) \tag{50}$$

$$(K|K\underline{+}2) = b_{K,K\underline{+}2} \, \Delta_{vK,vK\underline{+}2}$$

$$(K|K\underline{+}4) = b_{K,K\underline{+}2} \, b_{K\underline{+}2,K\underline{+}4} \sum_{v'} \frac{\Delta_{vK,v'K\underline{+}2} \, \Delta_{v'K\underline{+}2,vK\underline{+}4}}{W_{vK} - W_{v'K\underline{+}2}}$$

Koehler and Dennison[13] have shown that the quantities W_{vK} can be obtained

[13] J. S. Koehler and D. M. Dennison, Phys. Rev. 57, 1006 (1940).

from a continued fraction of the form

$$\xi = M_o - \cfrac{1}{M_{-1}-\xi} - \cfrac{1}{M_{-2}-\xi} - \cfrac{1}{M_{-3}-\xi} - \cdots$$

<div style="text-align:right">(51)</div>

$$- \cfrac{1}{M_{1}-\xi} - \cfrac{1}{M_{2}-\xi} - \cfrac{1}{M_{3}-\xi} - \cdots$$

in which

$$M_{\ell} = \frac{4s^2 F}{V_o} (\ell - g)^2, \quad \ell = 0, \pm 1, \pm 2$$

$$g = \left[(CK/F) - \varkappa) \right]/s, \quad \varkappa = 0, 1, 2, \ldots s-1 \qquad (52)$$

$$W_{nK} = \frac{1}{2} V_o' - \left[C^2 K^2 / F(C-D) \right] + s^2 f \, \xi$$

To calculate the Δ's continued fractions may also be used. The function $\mathcal{V}_{nK}$ is expanded in a Fourier series:

$$\mathcal{V}_{nK} = \sum_{m=-\infty}^{\infty} A_{nK,m} \, e^{im\alpha}$$

This is substituted in the differential equation (47) and leads to a set of simultaneous equations for the coefficients A:

$$A_{nK,m-s} + G_m A_{nK,m} + A_{nK,m+s} = 0$$

where

$$G_m = \frac{1}{2} M_e - 1 - (2Fs^2/V_o) \, \xi$$

These simultaneous equations yield the continued fraction

$$\frac{A_{nK,m+s}}{A_{nK,m}} = \cfrac{-1}{G_m} - \cfrac{1}{G_{m+s}} - \cfrac{1}{G_{m+2s}} - \cdots$$

The normalization condition

$$2\pi \sum_{m=-\infty}^{\infty} \left| A_{nK,m} \right|^2 = 1$$

enables the determination of the A's to be completed.

There will of course be an infinite number of roots for each value of K and $\mathcal{H}$. These roots are most conveniently calculated if none of the denominators $M_\ell - \xi - \ldots$ are small. If one of these should turn out to be small, the continued fraction should be transformed so that the offending M_ℓ appears in the leading position; i.e.

$$\xi = M_\ell - \cfrac{1}{M_{\ell-1} - \xi} - \cfrac{1}{M_{\ell-2} - \xi} - \ldots$$

$$- \cfrac{1}{M_{\ell+1} - \xi} - \cfrac{1}{M_{\ell+2} - \xi} - \ldots$$

(53)

For each root sought, there will be an appropriate choice of the leading term M_ℓ which will cause the most rapid convergence.

The various values of $\mathcal{H}$ yield the different component levels which in the limit of high barriers come together to form a (degenerate) harmonic oscillator level. However, Koehler and Dennison[13] showed that the roots are periodic functions of K (as may also be seen from Eq. 51) with period Fs/C. Furthermore, if this periodic function is known for the case $\mathcal{H} = 0$, it can be used to calculate the roots for the other values of $\mathcal{H}$ by a "phase shift," i.e. by reading off the value of ξ for

$$K' = K - F\mathcal{H}/C$$

from the same periodic curve used for $\mathcal{H} = 0$.

For sufficiently high barriers the dependence of ξ on K and $\mathcal{H}$ vanishes. This suggests expanding ξ as a Fourier series (only cosine terms will appear)

$$\xi = \xi_0 + \xi_1 \cos 2\pi g + \xi_2 \cos 4\pi g + \dots \quad .$$

For high enough barriers only a few terms are required. The coefficients ξ_0, ξ_1, ξ_2 can be found by solving the continued fraction for the necessary number of values of g, conveniently chosen to make it easy to solve for the required number of ξ's. The value of ξ_0 can also be obtained from available tables[11] by means of the relation:

$$\xi = \tfrac{1}{4} \, be_r(S) \quad \text{or} \quad \tfrac{1}{4} \, bo_v(S)$$

with
$$S = 4V_o'/s^2 f = 4V_o/s^2 F$$

Then the Δ's may be written

$$\Delta_{n'K',nK} = 2\pi \sum_{m=-\infty}^{\infty} {}' A_{n'K',m} \, A_{nK,m}$$

In some cases, especially when b is sufficiently low, the $(K|K\underline{+}4)$ elements of the secular equation (50) can be neglected altogether. However, this procedure is not always valid. Under such circumstances the secular equation can be made easier to solve by various transformations which reduce the order of the troublesome K,K$\underline{+}$4 elements so that they can be ignored and the remaining equation treated by the continued fraction method. These transformations are/similar to Van Vleck transformations but have to be adapted to the several cases which arise because of near-degeneracies and will therefore not be detailed here.